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STRUCTURE-PROPERTY RELATIONSHIPS IN THERMOPLASTIC ELASTOMERS. III.

SEGMENTED POLYACETAL-POLYURETHANES

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Structure-Property Relationships in Thermoplastic Elastomers. III.

Segmented Polyacetal-Polyurethanes

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glass transition temperature (T sub g)

Dihydroxy terminated polyacetals had been synthesized from aldehydes and glycols and used as soft segments to obtain segmented polyurethane block copolymers. For soft segment $\geq$ 1,700 $\overline{M}_n$, the T_g ranges from -48° to -58°C and is insensitive to the structures of diisocyanate and chain extender. The T_g of PacPU with 1,350 $\overline{M}_n$ *(M sub n)* polyacetals is raised to -38°C and none was observed for shorter polyacetal chains. The copolymers can be synthesized to have a broad range of mechanical properties such as modulus from 0.5 to 130 MPa, stress at break from 0.7 to 21 MPa and elongation at break from 66% to 1300% through the variation of the constituents and composition. The rheological properties are only slightly dependent on temperature for symmetrical diisocyanates but quite temperature sensitive with asymmetrical diisocyanate copolyemrs. The polyacetals are selected to build in acid catalyzed thermal decomposition of the thermoplastic elastomers. The hard and soft segments have TGA decomposition peaks at 292° and 343°C, respectively. Most copolymers display 2 peaks at temperatures between these two limits.

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INTRODUCTION

Block copolymers,[1] especially the segmented types, are quite amenable to molecular engineering. Our research has been directed toward establishing basic structure-property relationships for a variety of thermoplastic elastomers having contrasting physical, chemical and mechanical properties such as tough versus soft, thermally stable and unstable, low versus high melt viscosity, low and high T_g, amorphous versus crystalline hard segment, etc. We have reported structure-property relationships of segmented polyether-polyurethanes[1] and their thermochemistry.[2] The soft polyether segments is thermally more stable than the hard polyurethane segment and is insensitive toward acid catalyzed decomposition. In this paper we report the synthesis of a novel polyacetal soft segment which has the designed degradative characteristics and a wide range of physical and mechanical properties.

EXPERIMENTAL

Materials

Butyraldehyde was purchased from Fisher Scientific Co., diethyleneglycol and other aldehydes were from Aldrich Chemical Co. The aldehydes were treated with sodium carbonate, dried with sodium sulfate, and distilled twice before use. Diethyleneglycol was dried with molecular sieve and distilled before use. p-Toluene sulfonic acid was purchased from MCB, 4,4'-diphenylmethane diisocyanate (MDI) from Mobay Chemicals, 2,4-toluene diisocyanate (TDI) from Sigma Chemicals, and 2,6-toluene diisocyanate (TDI') from Aldrich

Chemicals were all distilled _in vacuo_ before use. The purity of TDI and TDI' were checked by IR absorption[3] at 910 cm^{-1} and 781 cm^{-1}, respectively. Bis-2-hydroethylisophthalamide (BI) and bis-2-hydroxyethylterephthalamide (BT) were synthesized by aminolysis of the isophthalate and terephthalate esters, respectively, with 2-aminoethanol. BI, m.p. 138-140°; analysis found (theoretical): C, 56.80 (47.13); H, 6.54 (6.39); N, 11.38 (11.11); BT, m.p. 232-233°C; analysis: C, 56.98 (57.13); H, 6.60 (6.39); N, 11.23 (11.11).

Solvent dimethylformamide (DMF) from Fischer Scientific was dried with molecular sieve and distilled in the presence of TDI under vacuum before use. Catalyst dibutyltindilaurate was purchased from Alfa Products.

Synthesis of Polyacetal

Polyacetals (Pac) were synthesized by the following scheme

$$RCHO + HOCH_2CH_2OCH_2CH_2OH \xrightarrow[\substack{Benzene \\ Reflux}]{P-TSA} HO(CHOCH_2CH_2OCH_2CH_2O)H + H_2O \qquad (1)$$

$$\underset{R}{} \qquad \underset{I}{}$$

R = Pr, Bu
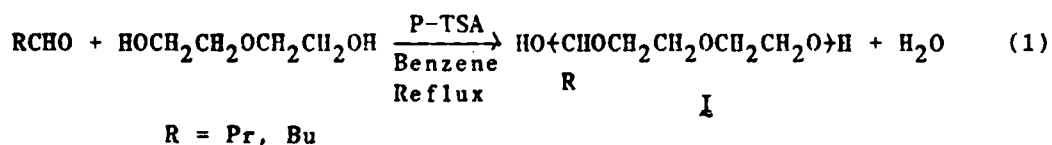
Equal moles of valeraldehyde, diethylene glycol, and 10^{-4} mole equivalent of TSA in benzene were reacted in a three necked flask equipped with mechanical stirrer, Dean Stark trap and condenser. After about 48 hrs reflux, 90-94% of theoretical yield of water was eliminated. The reaction mixture was washed with aqueous alkali solution and then with water to neutrality. After drying with Na_2SO_4, the lower boiling compounds were removed by distillation under reduced pressure with a yield of 82-90%. Number average molecular weight. $\overline{M}_n$, was determined by Karl-Fisher Method[4] to be 1350-1900. The properties of

various polyacetals are given in Table I.

Synthesis of Polyacetal Polyurethanes

The segmented polyacetal polyurethanes were synthesized from polyacetals derived from either butyraldehydes ($\overline{M}_n$ = 750) or valeraldehyde ($\overline{M}_n$ = 1,350-1,900) using the following reactions.

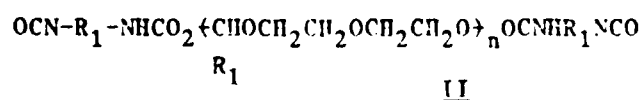Table I. Synthesis and properties of polyacetals[a]

$R-C{\overset{O}{\underset{H}{}}}$ R=	Reaction time, hr.	Yield %	$\overline{M}_n$ GPC[b]	$\overline{M}_n$ End group[c]	$[\eta]$,[d] dlg^{-1}	T_g, °C
H	20	96	1,300	1,290	0.15	-43
CH_3CH_2-	48	22	1,200	1,160	0.13	-77
$CH_3CH_2CH_2-$	48	33	750	720	0.10	-84
CH_3-C- CH_3	48	35	870	708	0.065	-76.4
$CH_3CH_2CH_2CH_2-$	48	82-90[e]		1,350-1,900		-74 to -76.8
$CH_3-CH-CH_2-$	20	95	2,000	1,900	0.13	-58
⬡—	20	80	940	820	0.074	-51

[a]All with diethylene glycol; [b]N-methylpyrrolidone solvent; [c]Karl-Fischer method using LiAlH$_4$; [d]Intrinsic viscosity in; [e]Range of values for different preparations.

$$HO(CHOCH_2CH_2OCH_2CH_2O)_nH + 2OCNR_2NCO \xrightarrow[\substack{50-60°C \\ 1 \ Hr \ DMF}]{BTL}$$

$$R_1$$
$$\underline{I}$$

$$\qquad (2)$$

$$OCN-R_1-NHCO_2(CHOCH_2CH_2OCH_2CH_2O)_nOCNHR_1NCO$$
$$R_1$$
$$\underline{II}$$

$$\underline{II} + HOR_3OH \xrightarrow[\substack{r.t. \text{ or} \\ 50-60^\circ C \ 4 \ hr.}]{DMF} \qquad (3)$$

$$\{CONHR_2NHCO_2\{CHOCH_2CH_2OCH_2CH_2O\}_nOCNHR_2NHCO_2R_3O\}_m$$
$$R_1$$
$$\underline{III}$$
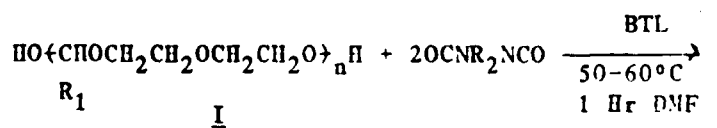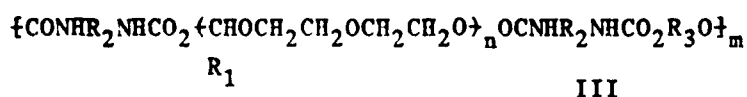
Ten gm of polyacetal was dropped into the DMF solution of diisocyanate, the mole ratio between polyacetal and diisocyanate was 1:2. 1 drop of dibutyl-tin dilaurate was added as catalyst. The reaction proceeded at 50-60°C for 1 hr in N_2 atmosphere, then the DMF solution of chain extender was added. The second step reaction was run at either room temperature or 50-60°C for 4 hr. The reaction mixture was then casted on Teflon sheet, and the solvent was removed at 80°C and 1 torr overnight. The PacPU yield is about 95%.

The MW of the polyurethanes was determined by a Waters Associates gel permeasion chromatograph. Tetrahydrofuran or N-methylpyrrolidone was used as solvent. The calibration curve was made with a series of standard polystyrene. The results of PacPU synthesis are listed in Table II.

Preparation of Nitrogen Substituted Polyurethane[5]

Five gm of polyurethane, Pac(7.5)-TDI-BI(1-2-1), was dissolved in 15 ml of DMF and a suspension of 0.48 g NaH in 5 ml DMF was added dropwise at -5°C. As hydrogen gas was evolved and the color of the solution turned to green, 0.36 g of C_2H_5Br was added and stirred for 1 hr at 0°C. The reaction mixture was poured into distilled water; the precipitated polymer was washed thoroughly with water then dried at 50°C and 1 torr overnight. 3.12 gm of a soft and somewhat sticky polymer was obtained. The product has $\overline{M}_n$ = 12,100

and $\overline{M}_w$ = 24,000; its IR spectrum is the same as the parent polyurethane except with a reduced NH absorption at 3300 cm^{-1}.

Instrumental Techniques

TGA was obtained with a Perkin Elmer TGS-II instrument using ca. 5 mg sample, with a nitrogen flow rate of 0.08 ml min^{-1} and 20°C min^{-1} heating rate. DSC curves were obtained with a Perkin Elmer DSC-II instrument at a 20°C min^{-1} heating rate.

Dynamic rheological properties were measured with a RD 7700 spectrometer using 2.5 cm diameter parallel disks, 10% strain at 10 rad. sec^{-1}.

An Instron Tester was used to measure the mechanical properties of solvent casted copolymer film. Residual DMF was removed by evacuation at 70-80°C, < 1 torr for more than 24 hr. The strain rate was 10 cm sec^{-1}.

Table II. Polyacetal polyurethane synthesis and some properties

| Copolymer[a] | Reaction Condition | | | | | GPC (THF) | | | |
| | Step 1 | | Step 2 | | | | | | |
	temp °C	time hr	temp °C	time hr	BC[b]	$\bar{M}n$	$\bar{M}w$	DP	Appearance
Pac(7.5)-TDI-BI	50-60	2	50-60	4	yes	14,900	26,900	1.81	not sticky elasticity no good
Pac(7.5)-TDI-BD	50-60	2	50-60	4	yes	17,800	42,300	2.38	slightly sticky elastic material
Pac(7.5)-MDI-BD	50-60	2	50-60	4	yes	13,900	25,000	1.80	not sticky no elasticity low streng
Pac(7.5)-MDI-BT	50-60	2	50-60	4	yes	14,200	27,700	1.95	not sticky less elasticity
Pac(7.5)-TDI-BT	50-60	2	50-60	4	yes	11,900	26,000	2.20	not sticky less elasticity
Pac(7.5)-MDI-BT	50-60	2	50-60	4	yes	23,800	40,100	1.68	flexible, no elasticity good streng
Pac(19)-MDI-BT	50-60	1	50-60	4	no	11,300	40,100	1.82	sticky elastic material
Pac(19)-TDI-BT	50-60	1	r.t.	4	yes	6,000	9,900	1.65	viscous liquid
Pac(19)-TDI-BT	50-60	1	r.t.	4	yes	11,200	15,500	1.35	very stick material
M-BT[d]	---	-	r.t.	4	yes	33,000[b]	45,000	1.36	hard brittl solid
Pac(19)-TDI'-BT	50-60	1	r.t.	4	yes	10,400[c]	14,000	1.38	not sticky elastic material

Table II (cont.)

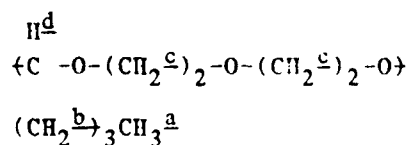|									
(19)-MDI[e]	50-60	1	---	-	yes	18,200	25,800	1.42	viscous liquid

c(7.5)-TDI-BI corresponds of Pac of 750 MW from butyraldehyde, 2 mole of TDI and 1 mole of all copolymers in this table have the 1:2:1 mole ratios of reactants; Pac(19) is 1,900 MW soft ment from valeraldehyde; [b]With or without benzoyl chloride (BC); [c]N-methyl pyrollidone is the vent for GPC; [d]Hard segment only polymer; [e]Soft segment polymer only.

RESULTS AND DISCUSSION

Synthesis

The MW of polyacetal synthesis is determined primarily by the
stoichiometry of the reactants and efficiency of removal of the byproduct
water. The latter was achieved by distillation of the azeotrope. In the case
of the butyraldehydes-water azeotrope, it has a boiling point of 68°C which is
lower than 69.4°C for the benzene-water azeotrope. This resulted in a low MW
polyacetal ($\overline{M}_n$ = 750). Attempts with parabutyraldehyde did not increase the
MW.

The boiling point of valeraldehyde-water azeotrope is 83°C. Higher MW
polyacetal can be obtained than butyraldehyde because of more complete
elimination of water. The ratio of aldehyde to glycol was 1:1. ^{1}H-NMR
spectra for the valeraldehyde-diethylene glycol polyacetal have peaks at
δ(ppm): $H^{\underline{a}}$ = 0.91, $H^{\underline{b}}$ = 1.40, $H^{\underline{c}}$ = 3.60, $H^{\underline{d}}$ = 4.56 in the correct intensity
ratio for

$$
\begin{array}{l}
H^{\underline{d}} \\
\text{+C } -O-(CH_2^{\underline{c}})_2-O-(CH_2^{\underline{c}})_2-O\text{+} \\
(CH_2^{\underline{b}})_3 CH_3^{\underline{a}}
\end{array}
$$

The IR spectra of MDI endcapped polyacetal of valeraldehyde-DEG has the
expected N-H stretching band at 3300 cm^{-1}, the N=C isocyanate vibration at
2260 cm^{-1}, the band at 1730 cm^{-1} for the C=O of isocyanate and a 1600 cm^{-1}
band for the carbonyl stretching of the urethane group. The IR spectra of the
corresponding TDI' capped soft block is like above except there are two

urethane C=O band at 1600 and 1620 cm^{-1} because of the two different urethane linkage with the 2,4-TDI. The spectra of the 1-2-1 copolymers of Pac-TDI-BI and the Pac-MDI-BD polymers have N-H band at 3300 cm^{-1}, a doublet C=O bands at 1710 and 1730 cm^{-1} and a doublet urethane C=O bands at 1600 and 1620 cm^{-1}. However in the case of the former polymer there is an additional intense absorption at 1650 cm^{-1}, which can be construed as absorptions due to allophenates.

The main side product is polyurethane synthesis is the allophenates found by the following reaction particularly at high conversion[6]

$$\underset{\displaystyle \wedge\!\wedge\!\wedge OC-NHR_2\wedge\!\wedge\!\wedge}{\overset{\displaystyle O}{\overset{\displaystyle \|}{}}} + \wedge\!\wedge R_2NCO \longrightarrow \wedge\!\wedge\!\wedge\ \underset{\displaystyle \underset{\displaystyle CONHR_2}{|}}{\overset{\displaystyle O}{\overset{\displaystyle \|}{O-C-N-R_2}}}\wedge\!\wedge\!\wedge \qquad (4)$$
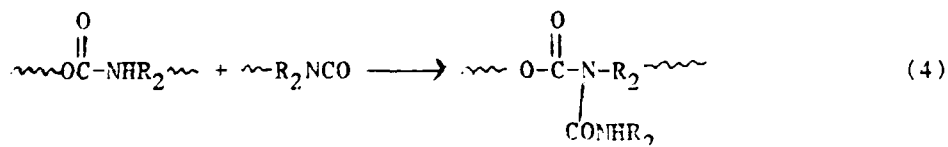
The presence of allophenate can be detected by its characteristic 1640 cm^{-1} IR band.[7] However, this assignment may not always be valid as Hocker[8] observed no 1640 cm^{-1} absorption in polymers containing allophenate groups. It is unlikely that the 1650 cm^{-1} absorption band in Pac-TDI-BI(1-2-1) polymer is assignable to allophenate because this absorption is absent in the spectra of Pac-MDI-BD(1-2-1) polymer. Instead the 1650 cm^{-1} absorption may be best attributed to the C=O vibration of the aromatic amide of BI.

Gel formation can occur during reaction 2 or 3 which depends upon the particular reactants. The probable cause is a trace amount of polyfunctionality in the polyacetal. Gel formation can be prevented by the addition of a trace amount of benzoyl chloride, a technique of restoring

stoichiometric balance which is well known for condensation polymerizations.
If the added benzoyl chloride over compensates the stoichiometric imbalance,
then it can significantly lower the MW. Some of the very low MW copolymers in
Table I may be attributed to this effect such as one of the TDI products.
The effect of benzoyl chloride also supports the absence of allophenate
formation which could cause gelation.

The PacPU with some of the hydrogen atoms on the nitrogen replaced with
ethyl groups by the reaction

$$\text{~CONH~NHCO}_2\text{~} + \text{NaH} \xrightarrow[-50°C]{\text{DMF}} \text{~CON~NHCO}_2\text{~} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{Na} \qquad\qquad\qquad\qquad (5)$$

$$\xrightarrow[0°C]{\text{EtBr}} \text{~CONEt~NHCO}_2\text{~}$$

The derivative is a very soft material due partly to reduced hydrogen bonding
interactions,[1] and the presence of ethyl groups both would detract from the
formation of crystalline domains.

Thermal Decomposition

In the previously reported polyether polyurethanes[1] the polyurethane hard
segment decomposes between 200 and 300°C before the polyether soft segment
decomposes above 400°C. The present copolymers also undergo two stage
decompositions as shown by the data in Table III, and the two TGA peaks in
Figure 1.

For the pure soft segment Pac(19) the first derivative TGA peak is at
343°C; the hard segment alone MDI-BI polymer has the peak at 292°C (Fig.
1c). Endcapping of the polyacetal definitely increases its thermal

stability; the Pac(19)-MDI has T_{50} and TGA peak (Fig. 1a) which are 66°

and 47°C higher than Pac(19), respectively. Under idealized situations, the

segmented block copolymers should undergo two stage decomposition with peaks

at 292°C and 390°C. Such is not the case; Table III shows that in general the

two TGA peaks lie between the two limits.

Table III. TGA data of polyacetal polyurethane

Copolymer (1-2-1)	Wt % of hard segment	T50[a] °C	TGA peaks °C[b] 1	2	H^{+} induced[c] wt. loss %
Pac(19)	0	314	343		98.0
Pac(7.5)-TDI-BI	44.4	311	298	340	31.4
Pac(7.5)-TDI-BD	36.9	317	339		41.0
Pac(7.5)-MDI-BD	44.0	315	not clear	340	38.0
Pac(7.5)-MDI-BI	50.1	337	315	348	
Pac(7.5)-TDI-BT	44.4	306	310	not clear	
Pac(7.5)-MDI-BT	50.1	318	304	330	
MDI-BI	100	309	292		
Pac(19)-MDI	11.6	380	390		39.9
Pac(19)-TDI-BI[d]	24.0	315	308	340	
Pac(19)-MDI-BI	28.4	338	316	366	32.0
Pac(19)-TDI-BI[e]	24.0	314	not clear	340	
Pac(19)-TDI'-BI	24.0	344	303	375	
Pac(15)-MDI-BI	33.4	–	–	–	33.4

[a]Temperature for 50% weight loss; [b]Obtained by first derivative of TGA
curve; [c]Acid catalyzed isothermal decomposition at 200°C for 20 min; [d]$\bar{M}_n$ =
13,300; [e]$\bar{M}_n$ = 6,000.

This may be partly attributable to imperfect microphase separation in the PacPU copolymers, but there is mixing-in-domain and/or domain mixing. This is supported by the sensitivity of thermal stability to the copolymer composition. For instance as the hard segment content decreases, the polymer becomes more thermally stable. In Fig. 1d of Pac(7.5)-MDI-BI(1-2-1) (50% hard segment) the TGA peaks are found at 336° and 360°C for the hard and soft segments, respectively. At lower hard segment content of 28% for Pac(19)-MDI-BI(1-2-1) (Fig. 1e), the two peaks at 347° and 366°C nearly merged. In this copolymer there may be little if any separate hard segment domain. If this hypothesis is correct then there should also be an effect from the structure of diisocyanate. This is indeed the case. Copolymers containing the asymmetric 2,4-TDI either have lower decomposition temperatures or have one of the two TGA peaks too weak to be resolved. In the case of both symmetric 2,6-TDI' and MDI, copolymers containing the former have the two TGA peaks approaching the limit values of the model soft and hard segments (compare Figs. 1e and 1f). This may mean better microphase separation in the 2,6-TDI' copolymers. There is apparently not a significant dependence on molecular weight. Thus, the two samples of Pac(19)-TDI-BI(1-2-1) denoted d and e in Table II, have $\overline{M}_n$ of 6,000 and 13,300 but the same hard/soft composition. They have very similar TGA curves.

Glass Transition

Polyacetals have very low T_g which is insensitive to MW. The values of T_g determined by DSC for polyacetals having $\overline{M}_n$ values of 750, 1,350, 1,500 and 1,900 are -76.0, -75.7, -74.1 and -76.8°C, respectively. This is raised by mere endcapping; for instance Pac(19)-MDI has T_g = -55.8°C. Microphase

separation is not expected for end-capped polyacetal. But polar interaction between end groups are apparently sufficient to lower the chain mobility. Table IV showed that the PacPU polymers all seem to have the same T_g between -48 and -58°C. There is no definite trend of T_g dependence on hard segment content, or the nature of the isocyanate and the chain extender. Though the

Table IV. T_g of PacPu copolymers

Copolymer	T_g, °C	Copolymer	T_g, °C
Pac(19)-MDI-BI(1-2-1)	-47.6	Pac(18)-TDI-BT(1-2-1)	-54.9
Pac(19)-MDI-BI(1-3-2)	-50.2	Pac(18)-TDI-BT(1-3-2)	-55.7
Pac(19)-MDI-BI(1-4-3)	-58.1	Pac(18)-TDI-BT(1-4-3)	-58.1
Pac(19)-MDI-BI(1-6-5)	-57.0	Pac(17)-MDI-BT(1-2-1)	-53.5
Pac(19)-TDI-BI(1-2-1)	-55.0	Pac(17)-MDI-Q(1-2-1)	-50.0
Pac(19)-TDI'-BI(1-2-1)	-50.4	Pac(17)-MDI-BD(1-2-1)	-50.8
		Pac(17)-MDI-BI1-2-1)	-50.1

T_g of Pac with 1,700 to 1,900 MW do not show significant differences, there is definitely a limit on soft segment chain length below which the low temperature T_g cannot be seen. This is true for the copolymer series with 750 MW polyacetal. In fact even with soft segment MW of 1,350, the Pac(13.5)-MDI-BI(1-2-1) has T_g raised to -37.9°C. The results suggest that the critical soft segment length is about eight repeat units.

Seefried et al.[9] studied the T_g of polyurethanes using dynamic mechanical measurements. They found that the polymers derived from 2,4-TDI have T_g

which increases with increasing hard segment whereas there is no comparable dependence for the corresponding MDI copolymers. In our copolymers the ones synthesized with 2,4-TDI and MDI have comparable T_g. This may be because the chain extenders we used are the more rigid BT and BI which tend to reduce the effect reported by Seefried et al. who used the flexible BD as the chain extender.

We were unable to observe any transition other than T_g including the melting transition which was found for polyether polyurethane[1] and other polyurethanes.[10] There is apparently extensive mixing of soft and hard segments in the domain boundaries,[11] or mixing of segments in their respective domains[1] so that there is no significant microphase separation. Wide angle x-ray analysis showed only a diffuse maximum at $2\theta = 20.5°$ suggesting the absence of any crystalline domain.

Rheological Properties

The rheological properties seem to be sensitive to the diisocyanate as might be expected. Table V compared them for copolymers comprising of the same polyacetal and chain extender but with different diisocyanates. The polymers containing the symmetric 2,6-TDI or MDI have complex viscosities, G' and G'' which are only slightly affected by temperature changes from 50° to 100°C. In marked contrast, these properties were decreased 2 to 3 orders of magnitude with the increase of 50° in temperature. Schneider et al.[12] reported extensive domain mixing in the 2,4-TDI polyurethanes but less mixing for the 2,6-TDI systems. Seefried et al.[9]

Table V. Rheological properties of PacPU copolymers

Copolymer	Temp., °C	η^*, poise	G', dynes cm^{-2}	G'', dynes cm^{-2}
Pac(19)-MDI-BI(1-2-1)	50	3.1×10^5	4.9×10^5	4.6×10^5
	100	6.7×10^4	2.7×10^6	1.4×10^6
Pac(19)-TDI'-BI(1-2-1)	51	1.0×10^5	6.2×10^5	1.2×10^5
	100	6.4×10^4	9.2×10^5	4.3×10^5
Pac(19)-TDI-BI(1-2-1)	50	5.8×10^4	2.9×10^5	5.0×10^5
	100	7.2×10^2	1.1×10^2	7.2×10^3

concluded that the symmetry of the diisocyanate influences the degree of order in the hard segment domain.

Mechanical Properties

PacPU segmented block copolymers can be synthesized to have a broad range of mechanical properties. Some of the stress-strain curves are shown in Figures 2 and 3. These properties at break and the moduli are summarized in Table VI. For very similar soft segments of $\overline{M}_n$ from 1,700 to 1,900, the molecular structures of the diisocyanate and the chain extender have profound effect on the mechanical strength of the material. For a given diisocyanate, the toughness decreases in the order of symmetric amide BT, bis(2-hydroxyethyl)hydroquinone, Q, nonrigid BD, and asymmetric BI. The 1-2-1 copolymer with asymmetric 2,4-TDI and BI is liquid like, while the strength increases with the symmetric 2,6-TDI' and BT. The modulus of the Pac-MDI-BI polymers increases at first with the hard segment content and then decreases after the latter exceeds 50%. This may be due to mixing of

segment segments into the hard domain. The same seems to be true for the 2,4-TDI-BT system even though materials with very high hard segment content was not prepared.

The copolymers have elongation from 63% to 1300%, and modulus from 0.5 to 129 MPa. Similarly large range of yield and break stress were found for the PacPU materials.

Table VI. Mechanical properties of PacPU copolymers

Copolymer	Hard Segment wt. %	$\sigma_{\underline{y}}$,[a] MPa	$\sigma_{\underline{b}}$,[b] MPa	$\varepsilon_{\underline{b}}$,[c] %	E,[d] MPa
Pac(17)-MDI-BT(1-2-1)	30.7		3.7	70.6	18.2
Pac(17)-MDI-G(1-2-1)	29.1		2.2	65.9	7.1
Pac(17)-MDI-BD(1-2-1)	25.8		1.5	145	2.8
Pac(19)-MDI-BI(1-2-1)	28.4	0.13	0.8	1300	0.46
Pac(19)-MDI-BI(1-3-2)	39.8	5.5	16.4	429	21.2
Pac(19)-MDI-BI(1-4-3)	48.0	12.9	20.6	378	129
Pac(19)-MDI-BI(1-6-5)	59.2	13.5	11.0	83.6	71.6
Pac(17)-TDI-BI(1-2-1)	26.1	0.07	--e	--	--
Pac(18)-TDI-BT(1-2.5-1.5)	31.1	1.9	14.3	907	11.1
Pac(18)-TDI-BT(1-3-2)	36.3	4.5	16.7	586	12.7
Pac(18)-TDI-BI(1-4-3)	44.7	13.2	25.9	385	86.1
Pac(19)-TDI'-BI(1-2-1)	24.0		0.7	90	4.2

[a]Yield stress; [b]Stress at break; [c]Extension at break; [d]Modulus; [e]Does not break.
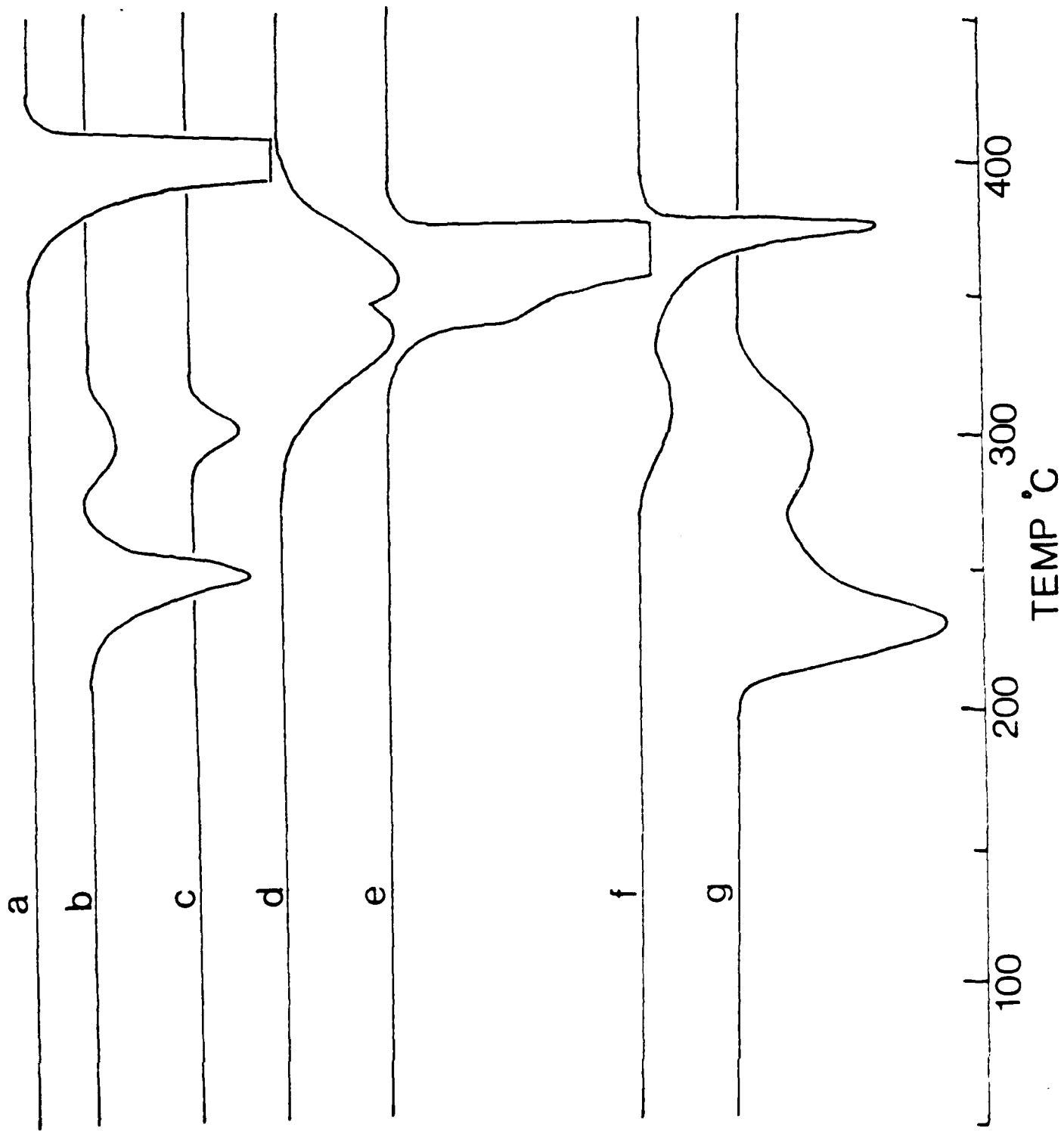
Captions for Figures

Figure 1.   First derivative of TGA curves for: (a) MDI-endcapped Pac(19)

with 11.6% hard segment; (b) same as (a) with 1% EtOTs; (c)

MDI-BI with no soft segment; (d) Pac(7.5)-MDI-BI(1-2-1)

50% wt. % hard segment; (e) Pac(19)-MDI-BI(1-2-1) 28.4% wt. %

hard segment; (f) Pac(19)-TDI'-BI(1-2-1) 24 wt. % hard
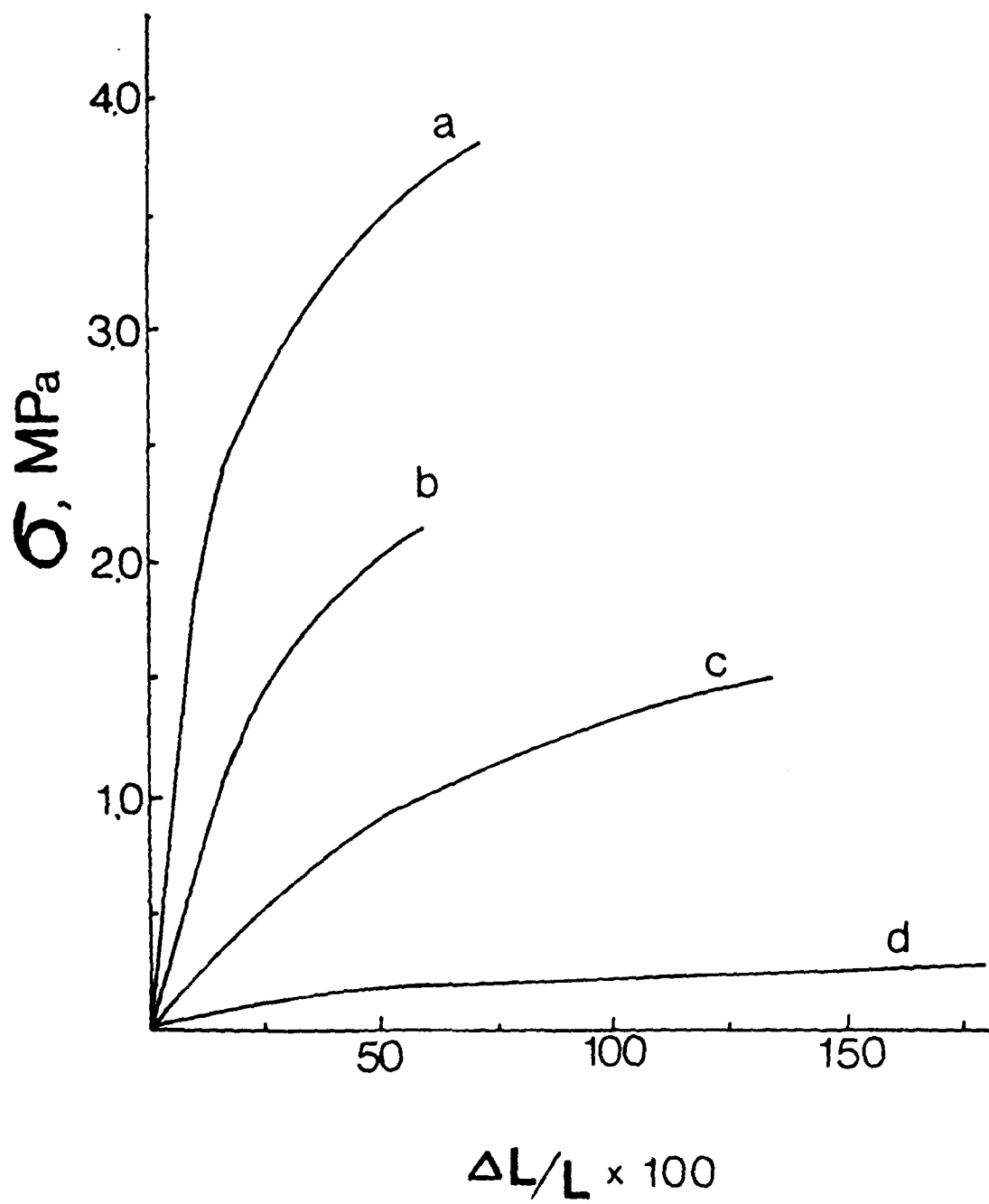
segment; (g) same as (e) with 1% EtOTs.

Figure 2.   Influence of chain extender on the stress-strain curve of: (a)

Pac(17)-MDI-BT(1-2-1); (b) Pac(17)-MDI-Q; (c) Pac(17)-

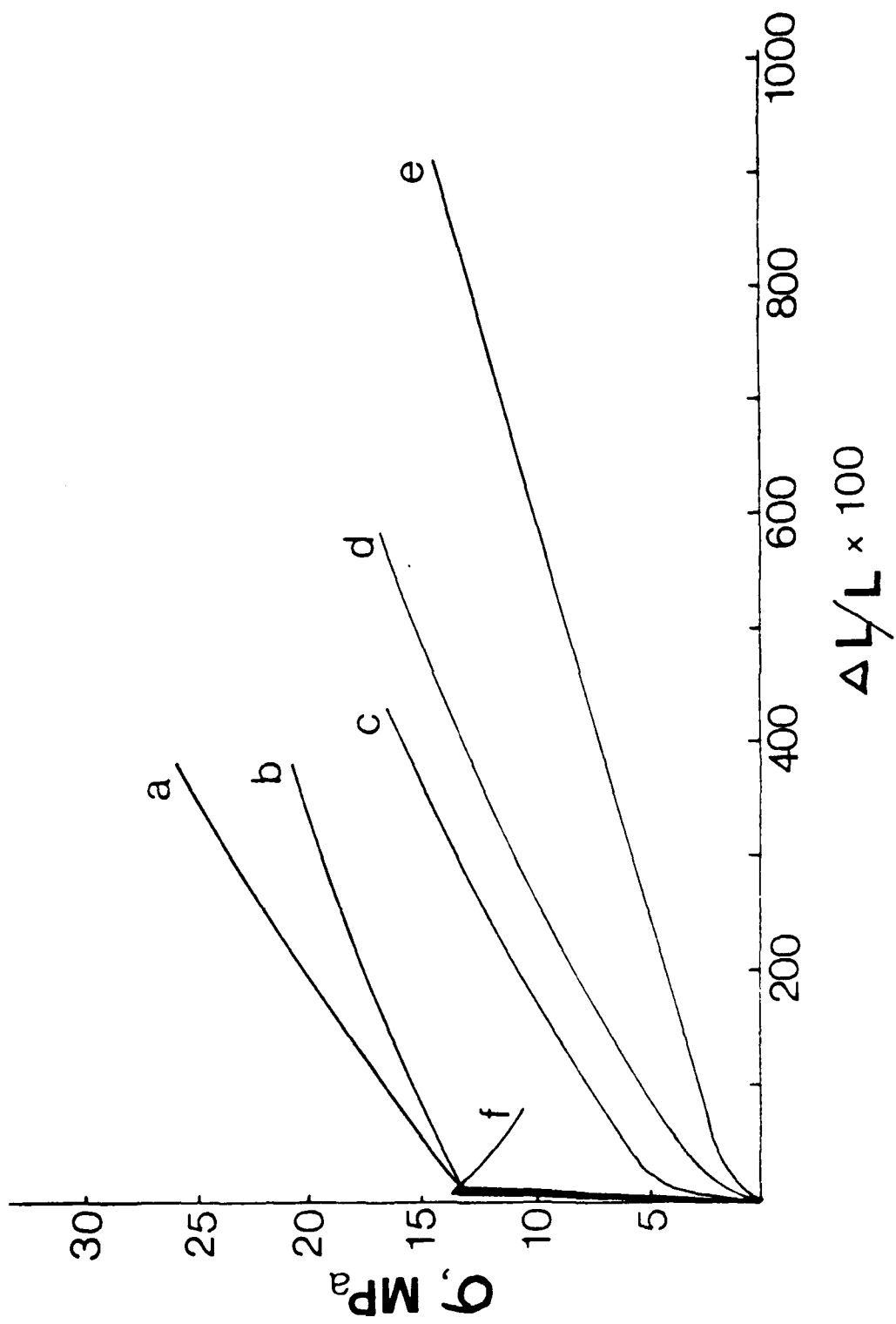MDIBD(1-2-1); (d) Pac(19)-MDI-BI(1-2-1).

Figure 3.   Stress-strain curves for two series of PacPU copolymers: (a)

Pac(18)-TDI-BT(1-4-3); (b) Pac(19)-MDI-BI(1-4-3); (c)

Pac(19)-MDI-BI(1-3-2); (d) Pac(18)-TDI-BT(1-3-2); (e)

Pac(18)-TDI-BT(1-2.5-1.5); (f) Pac(19)-MDI-BI(1-6-5).

REFERENCES

1. E.J. Woo, G. Farber, R. Farris, C.P. Lillya and J.C.W. Chien, <u>Polym. Engr. and Sci</u>. in press.

2. J.C.W. Chien and J.L. Fan, <u>Polym. Degrad. Stab</u>. in press.

3. D.F. David and H.B. Stanley, 'High Polymers', Vol. XVI, 'Analytical Chemistry of Polyurethanes' Part III, Wiley-Interscience, NY, 1969, p. 107.

4. G.A. Stenmark and F.T. Weiss, <u>Anal. Chem</u>. <u>28</u>, 1784 (1956).

5. H.C. Beachell and J.C.P. Buck, <u>J. Polym. Sci. Polym. Chem. Ed</u>. <u>1</u>, 1874 (1969).

6. G. Arzuino, A. Pino, O. Rossi and L.P. Friz, <u>J. Polym. Sci. Polym. Chem. Ed</u>. <u>13</u>, 1657, 1667 (1975).

7. P.J. Corish, <u>Anal. Chem</u>. <u>31</u>, 1298 (1959).

8. J. Ocker, <u>J. Appl. Polym. Sci</u>. <u>25</u>, 2879 (1980).

9. C.G. Seefried, Jr., J.V. Koleske and F.E. Critchfield, <u>J. Appl. Polym. Sci</u>. <u>19</u>, 3185 (1975).

10. G.W. Miller and J.N. Saunders, <u>J. Appl. Polym. Sci</u>. <u>13</u>, 1277 (1969).

11. T. Hashimoto, Y. Tsukahara, K. Tachi and H. Kawai, <u>Macromolecules</u> <u>16</u>, 848 (1983).

12. N.S. Schneider, C.S. Paik Sung, R.W. Matton and J.I. Illinger, <u>Macromolecules</u> <u>8</u>, 68 (1975).

a

b

c

d

e

f

g

TEMP °C

100   200   300   400

END

FILMED

7-85

DTIC